active, $[\alpha]_D$ −305°.

According to the literature [3], the melting point of L-canadine $C_{20}H_{21}O_4N$ is 133° C and its $[\alpha]_D$ is −299°, while DL-canadine melts at 170° C. The results of a direct comparison of the two substances, that with mp 166°–168° C and a sample of DL-canadine that we synthesized from dihydroallocryptopine, showed that they were identical. The IR spectra, (taken in alcoholic solutions on a SF-4 instrument in the 215–315 mμ region) of the chloride of the quaternary base and the base $C_{20}H_{21}O_4N$ obtained from it are similar to the spectrum of DL-canadine [4], which is confirmed by the following data.

Alkaloid	λ_{max}, mμ	log ε	λ_{min}, mμ	log ε
Quaternary base from				
Th. minus, chloride	231 (inflection), 286	3.99; 3.69	260	2.97
Base $C_{20}H_{21}O_4N$	230 (inflection), 285	4.06; 3.71	252	2.75
DL-Canadine	209, 230 (inflection), 284	4.45; 4.07; 3.71	252	2.76

Thus, the subsidiary alkaloid from Th. minus is identical with L-canadine β-methochloride. Although the initial mixture of alkaloid sulfates gives four spots on a chromatogram, only two alkaloids were obtained from it: β-allocryptopine and L-canadine β-methochloride. It is likely that this is due to the presence of stereoisomeric salts (asymmetrical with respect to the nitrogen).

REFERENCES

1. K. I. Kuchkova and G. V. Lazur'evskii, Izv. AN MoldSSR, ser. khim., 11, 43, 1965.
2. H. A. D. Jowett and F. L. Pyman, J. Chem. Soc., 290, 1913.
3. A. P. Orekhov, Chemistry of the Alkaloids [in Russian], Moscow, 387, 1955.
4. A. W. Sangster and K. L. Stuart, Chem. Rev., 65, 1, 69, 1955
5. K. Bauer, Die Organische Analyse [Russian translation], Moscow, 127, 1953.

15 August 1966

Institute of Chemistry, AS MoldSSR, Kishinev

ISOLATION OF ERVINIDINE AND ERVINIDININE FROM VINCA ERECTA

V. M. Malikov and S. Yu. Yunusov

Khimiya Prirodnykh Soedinenii, Vol. 3, No. 2, p. 142, 1967

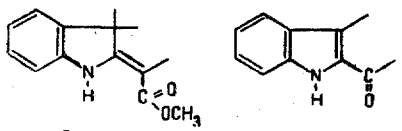
It has previously been reported that the alkaloids vincamine, reserpinine, erectine, ervamine, ervine, and akuammidine have been isolated from the epigeal part of Vinca erecta Rgl. et Schmalh, growing in the Fergansk Oblast [1–4]. Erectine was subsequently identified with the known alkaloid kopsinine [5]. Continuing the separation of the remaining part of the total alkaloids, we have isolated two new alkaloids: ervinidine with the composition $C_{22}H_{26}N_2O_4$ having mp 283°–284° C (decomp., methanol), $[\alpha]_D$ −17.3° (chloroform), and ervinidinine, $C_{21}H_{24}N_2O_3$, mp 255°–258° C (decomp., methanol), $[\alpha]$ −160.6° (methanol).

Ervinidine contains a methoxy group and a $=N-CH_3$ group and also one atom of active hydrogen. When ervinidine was oxidized by a modified Kuhn–Roth method, acetic acid was obtained, which shows the presence of a $C-CH_3$ group in the substance. The IR spectrum showed bands of vibrations at 3310 cm^{-1} (N–H bond), 1230, 1610, 1720 (the grouping $O-\underset{|}{C}=\underset{|}{C}-COOCH_3$), 1660 cm^{-1} (carbonyl group of a 2-acylindole nature). The information given showed that ervinidine has the following analytical formula:

$$C_{18}H_{19}(=NH)(=N-CH_3)(COOCH_3)(CO)(-O-).$$

Its UV spectrum contained three maxima: λ_{max} 232, 302, and 340 mμ (log ε 4.10, 4.08, 4.30, respectively).

The nature of the UV and IR absorption curves of ervinidine permit the assumption that the base can be assigned to the group of α-methyleneindolines (I) or 2-acylindoles (II) [6].



I II

To decide this question, ervinidine was reduced with sodium borohydride in methanol. This gave an amorphous base, ervinidinol, with R_f 0.43 [thin-layer chromatogram on silica gel, ethylacetate–methanol (9:1)], and 0.89 [paper chromatogram, butan-1-ol – acetic acid – water (100:5:100)]. The UV spectrum of ervinidinol had one maximum: λ_{max} 288 mμ (log ε 3.44) and a small break at 254 mμ (log ε 3.60) characteristic for an indole derivative.

The IR spectrum exhibited a broad band at 3350–3460 cm^{-1} (NH and OH), 1740, 1620, 1260 cm^{-1} ($COOCH_3$), and had no band in the 1660 cm^{-1} region (CO). The acetylation of ervinidinol gave an O-acetyl derivative (1760 cm^{-1}) although ervinidine does not acetylate. On the basis of these results, ervinidine can be assigned to the alkaloids of the 2-acylindole group. The structure of ervinidine is apparently close to that of picraphylline [7]. The UV and IR spectra and some chemical properties of the second base – ervinidinine are similar to those of ervinidine.

REFERENCES

1. P. Kh. Yuldashev, V. M. Malikov, and S. Yu. Yunusov, DAN UzSSR, no. 1, 25, 1960.
2. V. M. Malikov, P. Kh. Yuldashev, and S. Yu. Yunusov, DAN UzSSR, no. 4, 21, 1963.
3. S. Yu. Yunusov and P. Kh. Yuldashev, DAN UzSSR, no. 9, 23, 1956.
4. V. M. Malikov, P. Kh. Yuldashev, and S. Yu. Yunusov, KhPS [Chemistry of Natural Compounds], 388, 1966.
5. W. G. Kump and H. Schmid, Helv. Chim. Acta., 44, 1503, 1961.
6. J. A. Weisbach and B. Douglas, Chem. and Ind., 15, 623, 1965.
7. J. Levy, G. Ladouble, J. LeMen, and M. M. Janot, Bull. Soc. chim. Fr., 8, 1917, 1964.

4 November 1966

Institute of the Chemistry of Plant Substances,
AS UzSSR

A COMPARISON OF THE BJÖRKMANN LIGNINS FROM LARCH AND FIR WOODS

I. L. Shapiro, Yu. S. Pilipchuk, and R. Z. Pen

Khimiya Prirodnykh Soedinenii, Vol. 3, No. 2, pp. 143–144, 1967

The attempts that have been made repeatedly to investigate the chemical composition of larch lignin, in particular by Shorigina and Elkin [1], have shown that it is very similar to the lignins of other coniferous species of wood (in elementary composition and amount of functional groups). We have determined some physicochemical properties of larch lignin having a direct relationship with the processes of the delignification of the wood. We have studied the Björkmann lignin from Larix sibirica (OCH_3 15.04%, OH 13.10%, yield 20.9% for the Klason lignin in the wood). The material for comparison was a similar sample of lignin from Picea obovata (OCH_3 15.20%, OH 12.67%, yield 21.7%).

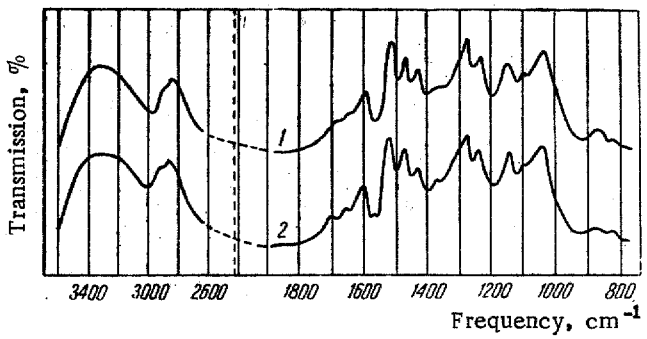


Fig. 1. IR spectra of the Björkmann lignins from larch (1) and fir (2).